Catena 173 (2019) 99–113

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

The waterlogged volcanic ash soils of southern Chile. A review of the "Ñadi" soils

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ARTICLE INFO

Keywords:
Aquands
Fraction analyses
Placic horizons
Land use-soil depth

ABSTRACT

The Ñadi soils (ÑS) is a local name for soils occurring at southern Chile (38° to 43° S) covering around 4250 km^2 hectares. Derived from volcanic materials, have discontinuous iron-cemented layers (the placic horizon) which favour waterlogging during the winter. The studies of iron-cemented layers are predominant in USA and Taiwan, but we provide an overview of ÑS research to position them within the group of soils with iron-cemented layers, and to highlight the distribution, formation, processes, and the relevance of placic horizons in land use and ecosystem services that ÑS provide.

We surveyed the worldwide literature of iron-cemented layers to put the Chilean soils with placic horizons. A fraction analysis was conducted in a longitudinal transect of five ÑS to evaluate the Si, Al, Fe and Mn reactive pools in the soil. A principal component analysis (PCA) was performed to separate the soil Series. Finally, a comparison between chemical properties of placic horizons and bog iron in Chile with other soils in the world was realised.

Further south, the Chilean ÑS have more SOC in surface horizons thus enabling more intensive iron translocation with the reactive soils pools decreasing with the latitude. The iron-cemented layers probably consist of goethite, ferrihydrite and gibbsite. A 51.8% of bog iron are compound of Fe while only 36.2% in the placic horizon, which also have 12.1% of Al_2O_3 in the molecular structure. Land uses in ÑS vary, from forestry to archaeology coexisting in these soils. In agricultural terms, we suggest a soil depth of 50 cm as the limit to drainage, shallower depth is at risk of severe soil degradation. Finally, several research questions are posed which may help to define the use and importance of the Ñadi ecosystem to the people who use the soils currently and to future generations within the context of climate change scenario.

1. Introduction

From the sedentary agriculture epoch (~11,000 BP) humans selected sites for cultivation according to soil properties (Brevik and Hartemink, 2010). Recent survey and classification of the soils provide more valuable information about the environmental conditions in which the soils evolved, which enables us to select the best sites for agriculture production. Diverse and complex interactions of the factors involved in soil formation (Jenny, 1941) generate many different agro-ecosystems in the world with a wide range of productivity (Sivakumar and Valentin, 1997). In Chile, the main agriculture areas are located in all longitudinal central valley (32–37° S), however for some crops (e.g. cereals and grasslands) the highest potential yields are reached in the southern-central regions (38–41° S), which are dominated by volcanic

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https://doi.org/10.1016/j.catena.2018.10.003
Received 6 November 2017; Received in revised form 2 October 2018; Accepted 5 October 2018
Available online 12 October 2018

Table 1
General information of Ñadi soil Series from longitudinal transect in Southern Chile.

Soil Series[a]	Soil taxonomy	Lat.	Long.	Soil colour	Soil texture[b]
Cunco	*Acrudoxic Hapludand*	38.9° S	72.1° W	10YR 2/2	Loam
Huiti	*Acrudoxic Duraquand*	39.9° S	72.7° W	10YR 3/2	Loam
Frutillar	*Typic Placaquands*	41.2° S	73.1° W	7.5YR 2.5/2	Silty clay loam
Alerce	*Duric Histic Placaquands*	41.4° S	73.1° W	7.5YR 2.1/1	Sandy clay loam
Calonje	*Histic Placaquands*	42.2° S	73.6° W	7.5YR 2.1/1	Silty clay loam

[a] Adapted from CIREN (2003). The classification systems used is USDA-NRCS.
[b] By feel in saturated conditions.

ash soils (Teuber, 1996; Calderini et al., 2011).

Besoaín (1985a) indicated that Chilean volcanic soils are derived from Pleistocene to Holocene volcanic materials dominated by intermediate tephra (Parada et al., 2010). Classified as Andisols (Soil Survey Staff, 2014) or Andosols (WRB, 2014) and locally they are called "trumaos", theses soils occurs in wide sector (86%) of southern Chile (IREN-UACh, 1978). A second group, Ultisols, (the "Red clayey soils") cover 13% of the land surface. The third soil group of importance in this area are the Aquands (waterlogged volcanic ash soils, locally called "Ñadi" from the native language: "seasonal swamp"). Ñadi soils (ÑS) are located in the central longitudinal valley between the Coastal Range and the Andean Range. Occur in plains between moraines glacial outwash landscapes (Sierra, 1982) and due to their limited soil depth suffer intense gleysation processes. According to Luzio et al. (1992), are characterised by a placic horizon (locally referred to as the "fierrillo") and above this horizon exhibit particular physical and chemical properties Dörner et al. (2017) and Pinochet et al. (2005): i) spatially variable soil depth, ii) phosphorus retention (> 85%), iii) very low bulk densities (< 0.65 Mg m^{-3}) and iv) high levels of soil organic carbon (SOC > 25%).

Although several studies have been conducted on volcanic ash soils (Ellies et al., 1993; Huygens et al., 2005; Matus et al., 2008; Dörner et al., 2010; Dec et al., 2012; Valle et al., 2015; Panichini et al., 2017); few are observed recently on ÑS (Besoaín et al., 1992; Grez, 1993; Janssen et al., 2004; Gerding et al., 2014; Dörner et al., 2016; Dörner et al., 2017). The aim of this review is to provide: i) a reference framework of soils with iron-cemented layers, ii) a conceptual description of formation of ÑS, iii) a fraction analysis of Si, Al, Fe, and Mn from Ap horizons in a longitudinal transect of ÑS in Chile. Finally, and according to the specific characteristics of Ñadi soils, we would like to iv) provide a dataset of placic horizons and sedimentary iron from southern Chile, v) to document of ecosystem services provided by these soils when they are subject to different land uses as well as vi) a list of new research questions related to these particular soils.

2. Material and methods

2.1. Information compilation

Using the main collection of Web of Science Core Collection (WoS-Thomson Reuters) and Google Scholar (https://scholar.google.cl/) we collected the data sets (using "placic horizons" as topic) to frame the iron-cemented layers in a global framework. The analysed database included documents, released between 1963 and 2018, starting with the first study of the Chilean ÑS during 1954, published by Díaz et al. (1958).

2.2. Sampling

During January 2016 a field trip in ~400 km transect was made (38.9° S–42.2° S) in southern Chile, considering cartographic units of five representative soil Series (Table 1) and under naturalised grasslands. After site description, three different samples (0–20 cm soil depth) in each site were stored in plastic bags and transported in cooler boxes to laboratory.

2.3. Laboratory analyses

All the soil samples were dried (~25 °C), later on were homogenised and sieved (< 2 mm) for the following chemical analyses: soil organic carbon (SOC), measured through wet combustion (Walkley and Black, 1934), soil pH$_w$ (in water 1:2.5), and exchangeable aluminium extracted with ammonium acetate at pH 4.8 (Sadzawka et al., 2006) were used to characterise the soils.

2.3.1. Selective dissolution methods

We used three selective dissolution reagents (oxalate, pyrophosphate and dithionite) to differentiate Si, Fe, Al and Mn forms in the soil transect as the basis for quantifying the reactive pools in the soils (García-Rodeja et al., 2004).

A solution of ammonium oxalate acid (0.2 M) at pH 3 was used in proportion soil:solution (1:50) for extraction of Si_o, Al_o, Fe_o, and Mn_o after 4 h of shaking in darkness. A Na-pyrophosphate (0.1 M) reagent was used in proportion soil:solution (1:100) for Al_p, Fe_p, and Mn_p linked to organic compounds after 16 h of shaking in darkness (Parfitt and Henmi, 1982). To both extractions, 4 drops of flocculant ("superfloc") were added and centrifuged (IEC Centra MP4, USA) at 3500 rpm by 10 min. At the filtered supernatant and by atomic absorption spectroscopy, the different elements were determined (SavantAA AAS-GBC, Australia).

A third extraction (dithionite) Si_d, Al_d, Fe_d and Mn_d linked to iron oxides was conducted (Mehra and Jackson, 1960) and 45 mL of citrate-bicarbonate solution were applied to 2 g of soil (sieved < 0.5 mm) Soil-solution was heated in a water bath (75 °C by 5 min) and 1 g of solid dithionite ($Na_2S_2O_4$) was added and shaken.[1] The 10 mL of saturated KCl solution was applied and heated during 5 min, being centrifuged and the supernatant spill in glass flask. The remaining soil follows the procedure described previously and a second supernatant is obtained. The elements are determined by AAS.

2.3.2. Images analysis

An analysis scanning electronic microscopy of placic horizon and bog iron was conducted. The samples were pre-treated with distilled water and shaken to clean off impurities. After, were covered with gold for enhanced resolution of the image. The sample was "sweep" by SEM (Carl Zeiss) and the peaks of elements were recorded.

2.4. Statistical analyses

For statistical analyses and graphs drawing, we used software STATISTICA 7.0 and GraphPad version 6.01 for Windows, respectively. For linear regression analyses among SOC and soil pH vs. Al_a, the fitting of goodness, determination coefficient (R^2), equation standard deviation (Sy.x) and residuals were calculated. Accumulated stocking bars plot were plotted to show the reactive pools in the soil. The data was

[1] The procedure was repeated two times.

normalised [(mean-observed value)/standard deviation] and then used in a principal component analysis (PCA) were conducted as an exploratory technique to discriminate between reactive specific fractions in the soil, to separate the groups of Ñadi soils along the longitudinal transect.

3. Results

A global perspective of soils with iron-cemented layers: (ortstein[2] and placic horizons).

In the framework searching of iron-cemented layers, we found 77 studies. Of these USA (16%), Taiwan (14%), Canada (13%), and Germany (8%) among others (Fig. 1). However, similar waterlogged soils with problems related to the presence of cemented layers (which are mainly composed of iron and aluminium), occur frequently (Lapen and Wang, 1999; Bockheim, 2011, 2014; Obear et al., 2014; Jien et al., 2016; Gomes et al., 2017) and are related to the influence of placic horizons in peatlands formation (Ugolini and Mann, 1979; Klinger, 1996). However, the available information of ÑS (Aquands) and placic horizons in international databases are scarce (Crampton, 1963; Alcayaga, 1964; McKeague et al., 1967; Lavkulich et al., 1971; Luzio et al., 1989; Besoaín et al., 1992).

Perhaps the first soil study presenting these conditions is reported by Senft (1862), in Germany, where the hard layers (ortstein horizons) are cemented by aluminium (ortstein horizon). Also, Vasili Dokuchaev in 1879 described the podsolisation processes in Russia, linking to the movement through the soil profile of aluminium and iron complexed with soil organic matter (Muir, 1961).

In North-America, Crompton (1952) and Crampton (1963), described the presence of thin iron pans related to podsolic soils, while McKeague et al. (1967, 1968) linked these processes to the translocation of iron and manganese in reduced conditions ($Fe^{2+,\,3+}$ and $Mn^{2+,\,3+}$). Miles et al. (1979); McKeague and Wang (1980) indicated that ortstein horizons were cemented with aluminium and are more linked to an organic complex than to iron. These results also prove that: i) not all cemented materials (e.g. ortstein) are related to iron oxidation processes and ii) podsolization processes do not always lead to the formation of placic horizons.

In the compilation made by Bockheim (2014), suggest that the formation of placic horizon requires high precipitation levels (2400–3900 mm $year^{-1}$), occurring frequently in depression positions in the landscape where the drainage is restricted by soil-lithic discontinuity. These conditions allow the formation of soil profiles characterised by organic-rich horizons near the surface, textural discontinuity, slowly permeability, and low pH values (Lapen and Wang, 1999; Pinheiro et al., 2004; Bockheim, 2011). Investigations made by Lapen and Wang (1999) on placic horizons showed that the iron cementation processes are facilitated by minimum root activities in cemented layers. Wu and Che (2005) and Jien et al. (2016) indicated that the formation of the placic horizon requires carbon sequestration for the mobility and chemical bounding of sesquioxides to translocate phosphorus to the Bsm horizon. In contrast, Obear et al. (2014) link the formation of the placic horizon to irrigation management and iron fertilisation.

In addition, the placic horizons could be related to microorganism activity. Trolard and Bourrié (2008) denoted that redox processes in the soil influence the presence or absence of iron, as cemented layers. Furthermore, Taylor and Konhauser (2011); Templeton (2011); and Joshi (2014) described that in extreme environmental conditions some groups of chemoautolithotrophic bacteria (e.g. *Thiobacillus ferrooxidans*) are able to oxidise iron under aerobic and anaerobic conditions.

The placic horizons occurs in different soil Orders, (e.g. Inceptisols in Taiwan, Histosols and Spodosols in USA and Canada) but are very

[2] From German “Stone place”.

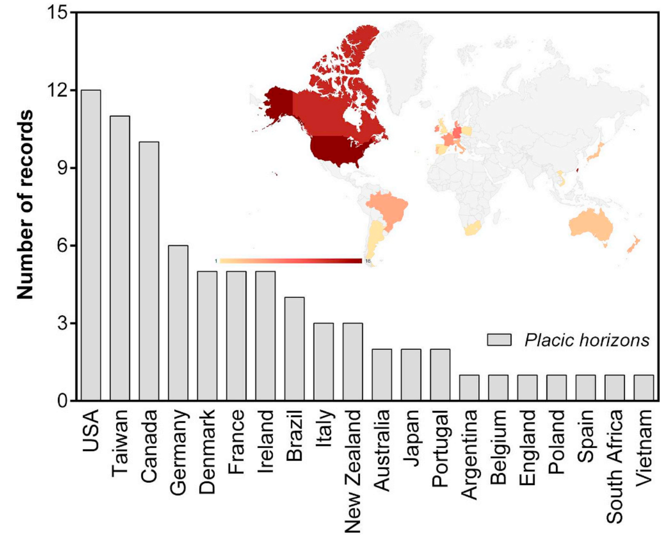

Fig. 1. Global distribution of placic horizons studies in WoS-Thomson Reuters and Google Scholar data base (1963–2018). Bars indicate records and world map the percentage.

commons: i) in volcanic ash soils (Shoji et al., 1988) with different land covers (coniferous forest, taiga, grasslands, shrubs, ferns, peatlands) and ii) over various parent materials (glacial till, sandy materials, loess, granite). However, new perspectives related to the placic horizons and soil functions (e.g. as an ecological indicator), land covers dynamics and ecosystem services has been considered in the future perspectives.

3.1. *The waterlogged volcanic ash soils. The Ñadi soil case*

In Chile, these soils have been investigated since 1954 (Díaz et al., 1958). The focus has been on the evaluation of the potential production capacity of these soils in order to calculate the correct value of the land for tax purposes. These soils were classified as a new group of volcanic soils, as reported by Wright (1965) and Beinroth et al. (1985). Geographically (Fig. 2) these soils are distributed from 38° 30′ to 43° 00′ S (Besoaín, 1985b; Ramírez et al., 1996; Teuber, 1996).

According to Köppen-Geiger climate classification (Kottek et al., 2006), these soils developed in warm temperate climates (Cfb) so that, geographically can be found in zone with increasing in the accumulated precipitation and diminished mean temperature as can be seen on the transect from Cunco to Calonje (Fig. 3A). These climate patterns favour SOC accumulation and pH values lower than 5.5 in the Ap soil horizons (0–20 cm).

The longitudinal transect shows pseudo-Ñadi[3] (as Cunco) and Ñadi soil Series. It covers Acrudoxic Hapludand (Cunco) to Histic Placaquands (Calonje). We observe a strong correlation between SOC and soil pH ($r = -0.90$) in the transect. As we forward to south, the SOC increases from 13 to 30%, which is reflected in the histic epipedon and in a progressive acidification from pH 5.5 to 4.4, reflected in Alerce and Calonje soil Series. The soil reactivity (Al_a) didn't show a good correlation with SOC (Fig. 3B; $R^2 = 0.64$), suggesting that in ÑS the pool of reactive of Al is partially related to SOC. These variations are reflected in the residuals plot (Fig. 3C), particularly in the Huiti and Frutillar soil Series. Díaz et al. (1958) mentioned that Frutillar soil Series (Typic Placaquand) which covers 5425 ha, it has been the ÑS with the most agricultural use in southern Chile, favoring their SOC mineralisation.

[3] Pseudo-Ñadi: Correspond to soils that developed in Ñadi zone, but the iron layer is not completely cemented so, the placic horizon is it not always formed or present.

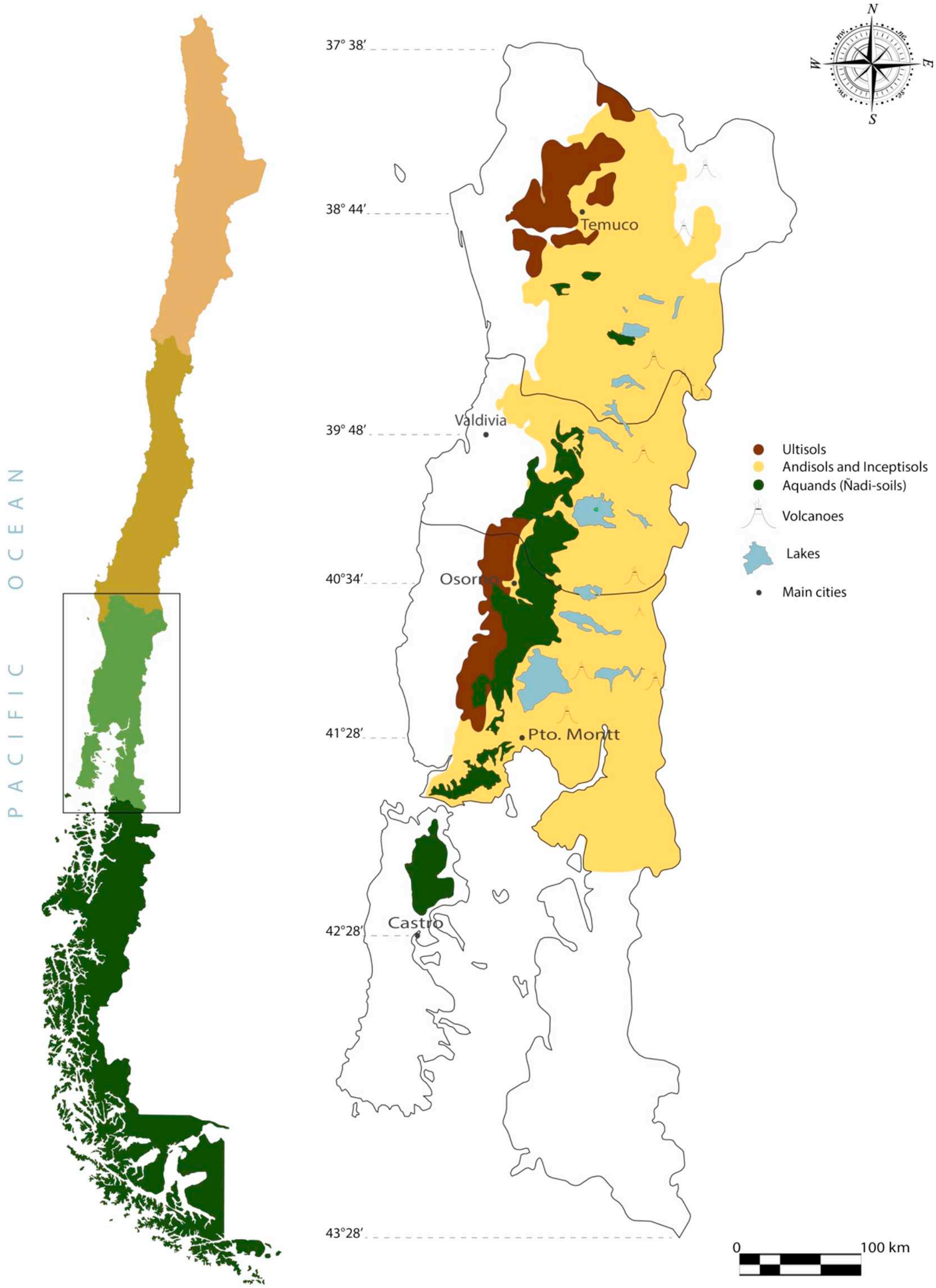

Fig. 2. Geographic distribution of ñadi soils (in green), mature volcanic ash soils (in yellow) and red clayed soils (in brown) in southern Chile. Map accommodated to Wright (1965) and Matus et al. (2006). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.1.1. Fractionation of reactive pool in Ap horizons in Ñadi soil transect

The reactive forms of Si, Al, Fe and Mn are presented in Fig. 4. These forms are the main factor of many properties (physicals and chemicals) of Andisols (García-Rodeja et al., 2004).

We appreciate that the reactive pools decreased towards the south in all extractions. In decreasing order, the relevance of the elements is Al > Fe > Si > Mn. In general, the extraction with oxalate shows the highest values (Cunco: 3.93% to Calonje: 0.69%), however in Cunco Series $Al_d + Fe_d + Mn_d$ related to iron oxides represent 4.25% of the reactive pool. In the Frutillar soil Series Al_p and Al_o have 2% of participation in the reactive pool, meanwhile in Alerce and Calonje the Al_p represents 1.71% and 0.93% of the reactive pool respectively. The latter suggests the relevance of organic complexes in the soil reactivity.

A principal component analysis (PCA) for the different reactive pools in the ÑS transect is presented in Fig. 5. In overview, the oxalate and dithionite-citrate-bicarbonate extractions explain 72.66% of the datasets variation while pyrophosphate and SOC explain 14.81% of the variation. Furthermore, we observe a clear separation of soil Series

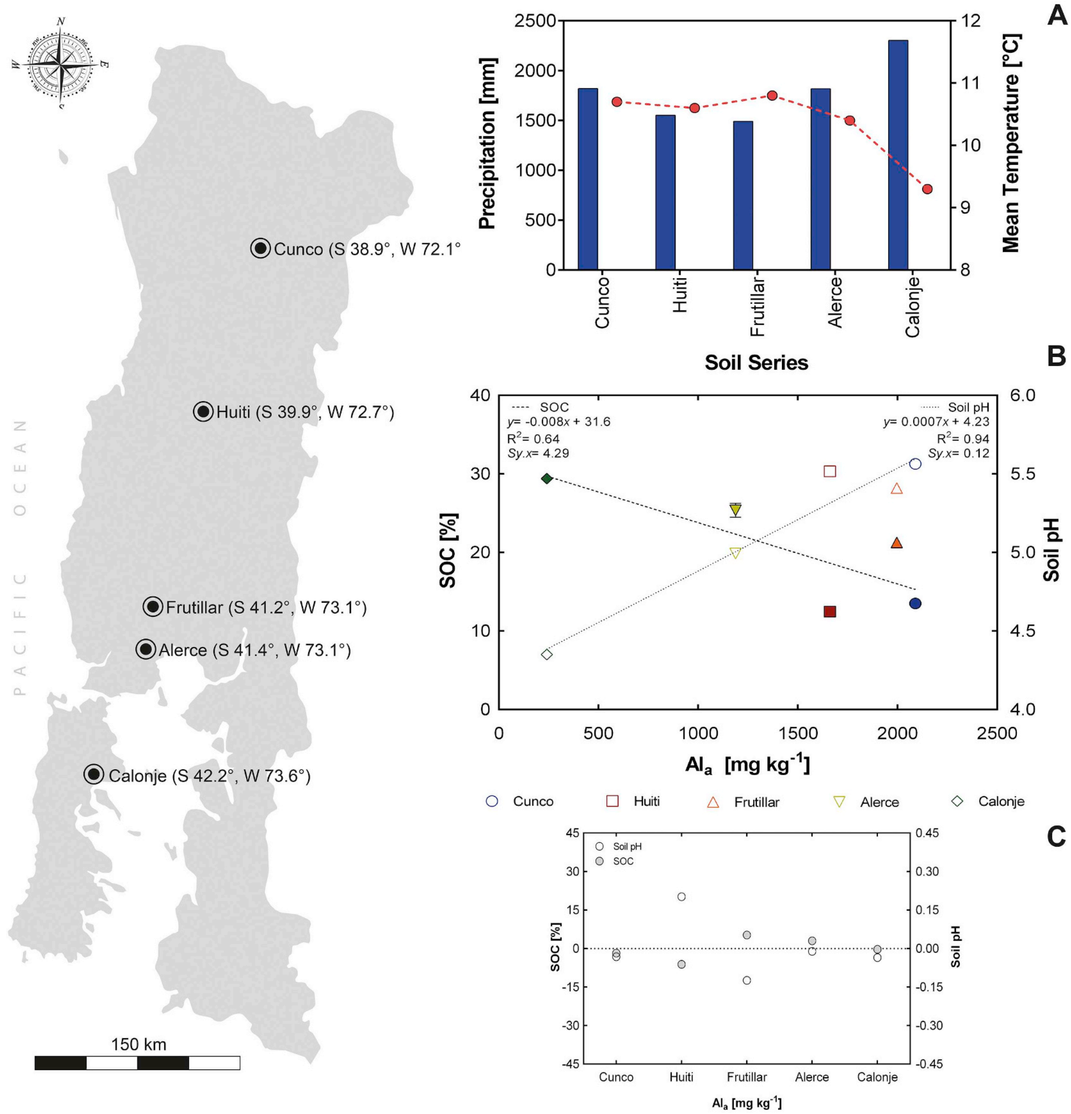

Fig. 3. Longitudinal transect of the ñadi soil Series in southern Chile. Left: Map with sampling sites. Right: A. Climate patterns for year 2017 of the longitudinal transect (from www.agromet.inia.cl). B. Linear regression between SOC vs. Al_a (fill symbols) and pH vs. Al_a (open symbols). C. Residual plots of SOC and pH of the ñadi soil Series.

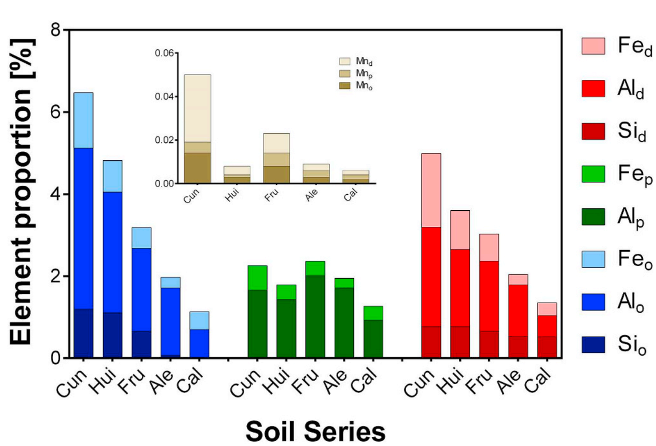

Fig. 4. Accumulated distribution of Si, Al, Fe and Mn in oxalate, pyrophosphate and dithionite-citrate-bicarbonate extractions through the longitudinal transect.

from Cunco to Calonje (Fig. 5A).

The Cunco soil Series is positively related to Al_o, Si_o (Fig. 5B) and Fe_d, Mn_d (Fig. 5D) and negatively with pyrophosphate extractions and SOC (Fig. 5C). Huiti soil Series is related to Mn_o, Fe_p and Al_d while Frutillar is strongly positively with SOC and Al_o, Al_d (Fig. 5B, C and D). Finally, Alerce and Calonje soil Series showed positive relation with SOC, however, Alerce is linked with Al_p and Mn_p and Calonje with Fe_p (Fig. 5C).

3.2. Formation of Ñadi soils

The original meaning of Ñadi (an Araucanian concept) is a broad ecological concept, that refers to poor drainage conditions, low altitude, dense temperate rain forest cover and firm but shallow soil profiles (Figs. 6 and 7A) (Wright, 1965).

Regarding the origin of these soils in Chile, Alcayaga (1964) indicated that ÑS were developed under cold and humid conditions with highly acidifying vegetation (e.g. coniferous) in the intermediate depression between the coastal range and the cordillera (Fig. 6A). Under this climatic regime successive deposits of volcanic ashes over a fluvi-

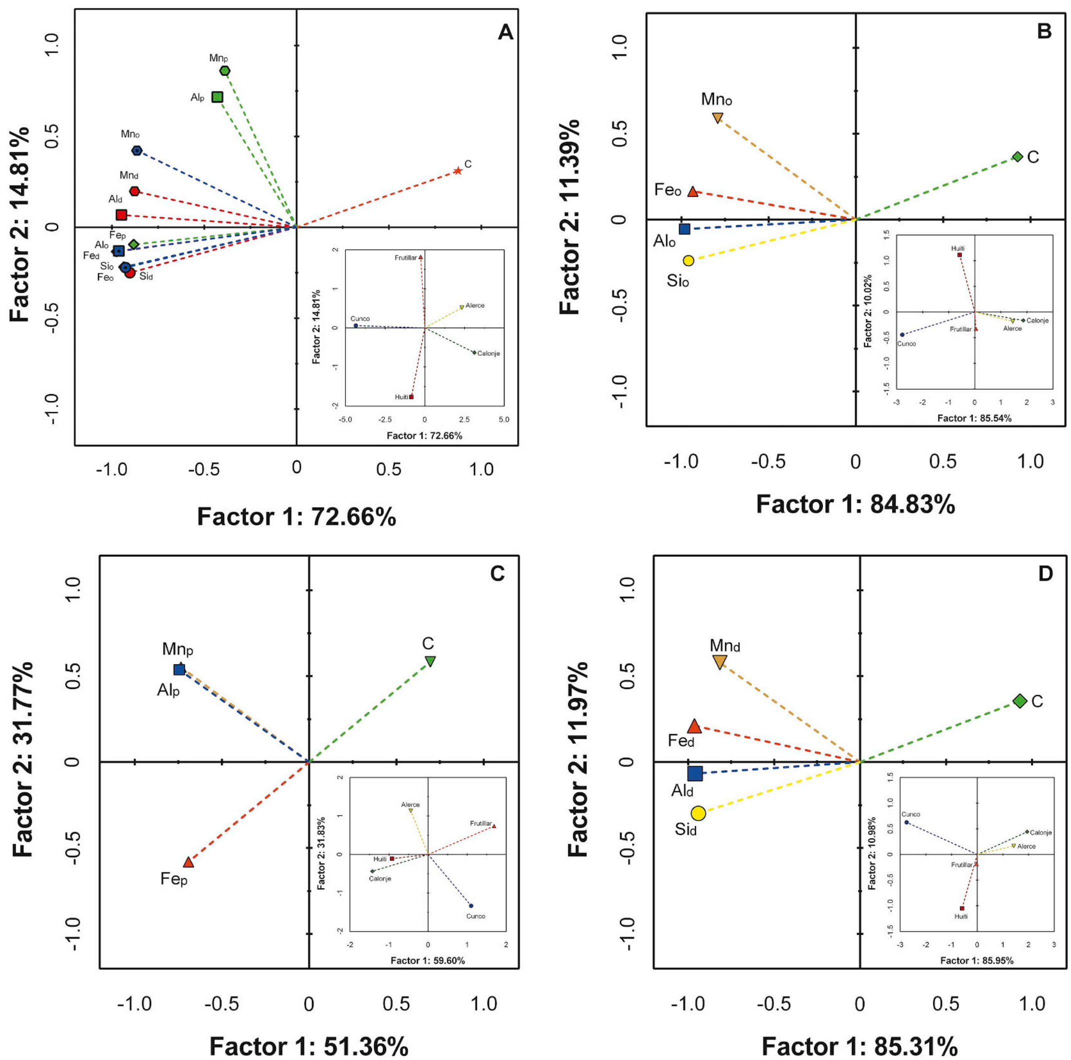

Fig. 5. Principal components analyse (PCA) considering A: All selective dissolution methods. B: Oxalate. C: Pyrophosphate and D: Dithionite-citrate-bicarbonate. Inset indicates the soil Series positions.

glacial or alluvial substratum occurred (Fig. 6B), which was cemented by silica, aluminium and iron (Wright, 1965; Besoaín et al., 1992). Later, these volcanic ashes evolved under warmer conditions and favoured the growth of less acidifying vegetation (e.g. grasslands). This process occurred during the Pleistocene (2.5 M yr–11,500 yr BP) (D'Amico et al., 2016). During the Holocene, volcanic ashes were deposited over the older buried A horizon (Fig. 6B), which under temperate and humid conditions, favoured the growth of ancient native forest (e.g. *Nothofaghus*). This forest was the dominant vegetation of these soils before an intense land use change, which has taken place in the last 500 years (Lara et al., 2012). According to Wright (1965), it is possible to find a thin iron-pan at the original B-horizon, which was defined as "fossil Ñadi soils".

3.2.1. *Properties of Ñadi soils*

These soils have particular physico-chemical properties characterised by high levels of SOC (approximately 25 to 30% in O horizons). The ÑS could be described as having a histic epipedon, but it does not always reach the thickness required for such a diagnosis. These soils exhibit high contents of soluble iron (Fe^{2+}) and aluminium (Al^{3+}) near the surface that are complexed with fulvic acids (Fig. 6C), which favours the accumulation of SOC (Silva and Schaefer, 1971).

The bulk density is very low (0.2–0.6 $Mg\,m^{-3}$), which is directly related to the SOC accumulation (Casanova et al., 2013), allowing an increase of N mineralisation and microbial immobilisation (Urbina et al., 1969, 1971). In deeper horizons iron and manganese oxides precipitate (Fe^{3+}, Mn^{3+}) and form a placic horizon or "fierrillo" (Luzio et al., 1992). The very low bulk density implies the soil has a high water holding capacity; however, this property is restricted due to the limited soil depth (Haller et al., 2015; Dörner et al., 2016; Carrasco et al., 2017). On the other hand, the high water repellent nature of the soil after periods of intensive drying also restricts its water holding capacity (Orellana et al., 2004; Dec et al., 2017).

3.2.2. *The placic horizon (Bsm) or "fierrillo"*

The iron accumulation is seen as a discontinuous placic horizon (1–4 mm thickness) located at the cemented substratum (Fig. 7C, E). This accumulation on the fluvial-glacial substratum is generated by the translocation of iron, silica, manganese and aluminium compounds linked to soil organic matter and precipitation. In the first stage, under cold, humid and waterlogged conditions, the O_2 concentration is low (reduced conditions) (D'Amico et al., 2016). The microorganisms that live in anaerobic soil use Fe^{3+} or iron oxides (Fe_3O_2) as terminal acceptors of electrons in the respiratory chain as a substitute for O_2. Thus, the Fe^{3+} is reduced and mobilised as Fe^{2+} within the soil profile. In aerobic conditions the microorganisms secrete chemical molecules (siderophores) chelating the Fe^{3+} (Fig. 6C) (Mengel and Kosegarten, 2005; Ahmed and Holmström, 2014). Such processes are linked to

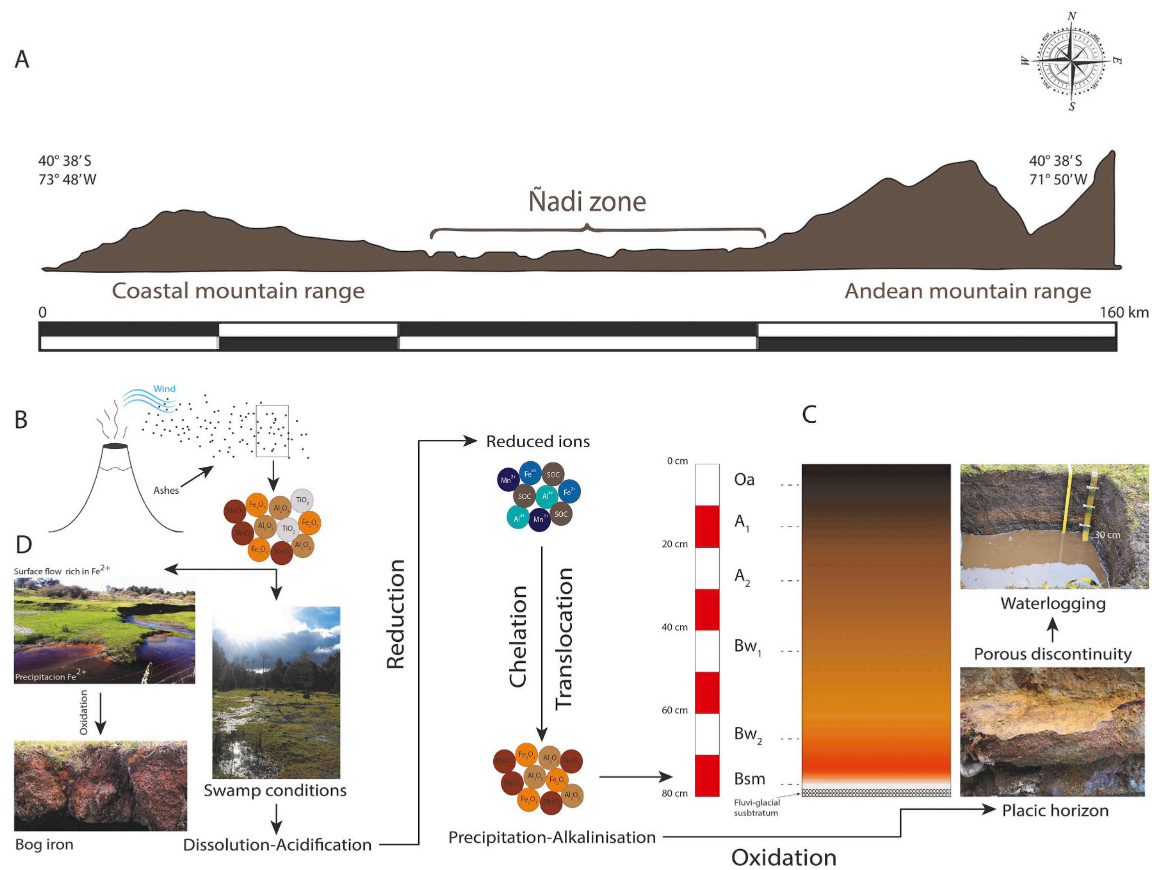

Fig. 6. Conceptual diagram formation of ñadi soil. A: Cross-section of Chile at to 40° 38′ S highlighting the "ñadi zone" (Adapted from Wright, 1965). B: Lithogenic iron derived from volcanic ashes deposited in swamp conditions. C: Schematization of placic horizon formation and typical ñadi soil profile. D: Lithogenic iron that was transformed in bog iron ore.

redox potential (E_h), pH, moisture, temperature and soil organic components (Luzio et al., 1989; Luzio and Saavedra, 1992; Besoaín et al., 1992).

In general, Fe^{2+}, Mn^{2+} and Al-humus components are translocated through the soil profile, above the Bsm horizon where pH < 5; E_h < 350 mV, until they reach the oxidation zone, (below Bsm: pH > 5; E_h > 350 mV). This is intensified by fluvi-glacial substrata which normally present a sandy matrix (Luzio et al., 1989; Lapen and Wang, 1999; Inglett et al., 2005).

At this horizon the reduced components are oxidised and deposited because of higher redox potential. This process probably takes place in warm conditions; therefore D'Amico et al. (2016) suggested that the presence of the Bsm horizon could be used as an indicator of the Quaternary period when the placic horizon ("fierrillo") (Besoaín et al., 1992) was formed. The "fierrillo" always shows a dark fringe rich in Mn, above the precipitated Fe in the placic horizon, dominated by minerals as ferrihydrite, goethite and lepidocrite (Campbell and Schwertmann, 1984) and some traces of gibbsite (Besoaín et al., 1992); are compound mainly by 36.2% of Fe, 12.1% of Al_2O_3 and some traces (0.7%) of Ti (Fig. 7E). Consequently, in ÑS, placic horizons can be seen as the combined effect of physical waterlogging and redox processes (Besoaín et al., 1992).

Chemical properties of iron-cemented layers from southern Chile are presented in Table 2. The bog iron layer was yielded highest crystalline forms (24.817%) that also is reflected in high content of Fe in the molecular structure (Fe = 51.8%, Fig. 7F). In the placic horizon the relationship Al_o-Al_p = −0.248%, suggests that the Bsm contain Al that comes from organic compounds from surface soil horizons (Ap as was showed in the Fig. 5C).

The SOC was 0.58% in bog iron and 0.25% in placic horizon and pH NaF was 8.23 in bog iron and 10.09 in placic horizon, suggesting that Bsm have a more reactive surface that bog iron.

Irrespective of whether the iron derives from volcanic materials or not, due to the high spatial variability and the dominant influence of geomorphological processes, the nature and origin of the iron oxide layers remains diverse. Bricker et al. (2004) stated that if iron is transported by superficial run off and re-deposited in depression sites as "stagnant water", it is called bog iron. This process could have caused the iron-cemented layer present in the archaeological site "Monte Verde" (Fig. 6D, 7D, F) that probably are dominated by goethite and hydrous ferric oxyhydroxide as ferrihydrite (Landuydt, 1990; Bricker et al., 2004). In the early Middle Ages this bog iron ore ("Raseneisenerz") was used to make tools and houses as well as churches and walls were built using iron stones. Thus, the use of bog iron influenced the culture and heritage of regions like Brandenburg and the heathland of Germany (Sitschick et al., 2005).

3.3. Land cover/use of Ñadi soils and related ecosystem services

Ecosystem services are defined as "*the beneficial flows arising from natural capital stocks which fulfil human needs*" (Dominati et al., 2010, p. 1859). Changes in the ecosystems can be linked to soil functions and the ecosystem services that are provided.

Considering arable and no arable land, ÑS in southern Chile cover around 4250 km^2 (ODEPA, 1968a, 1968b). Approximately 40% of this area (170,000 ha) has a seasonal agricultural or forestry use, which implies ecosystem services such as the food, wood or fibre provision (Teuber, 1996).

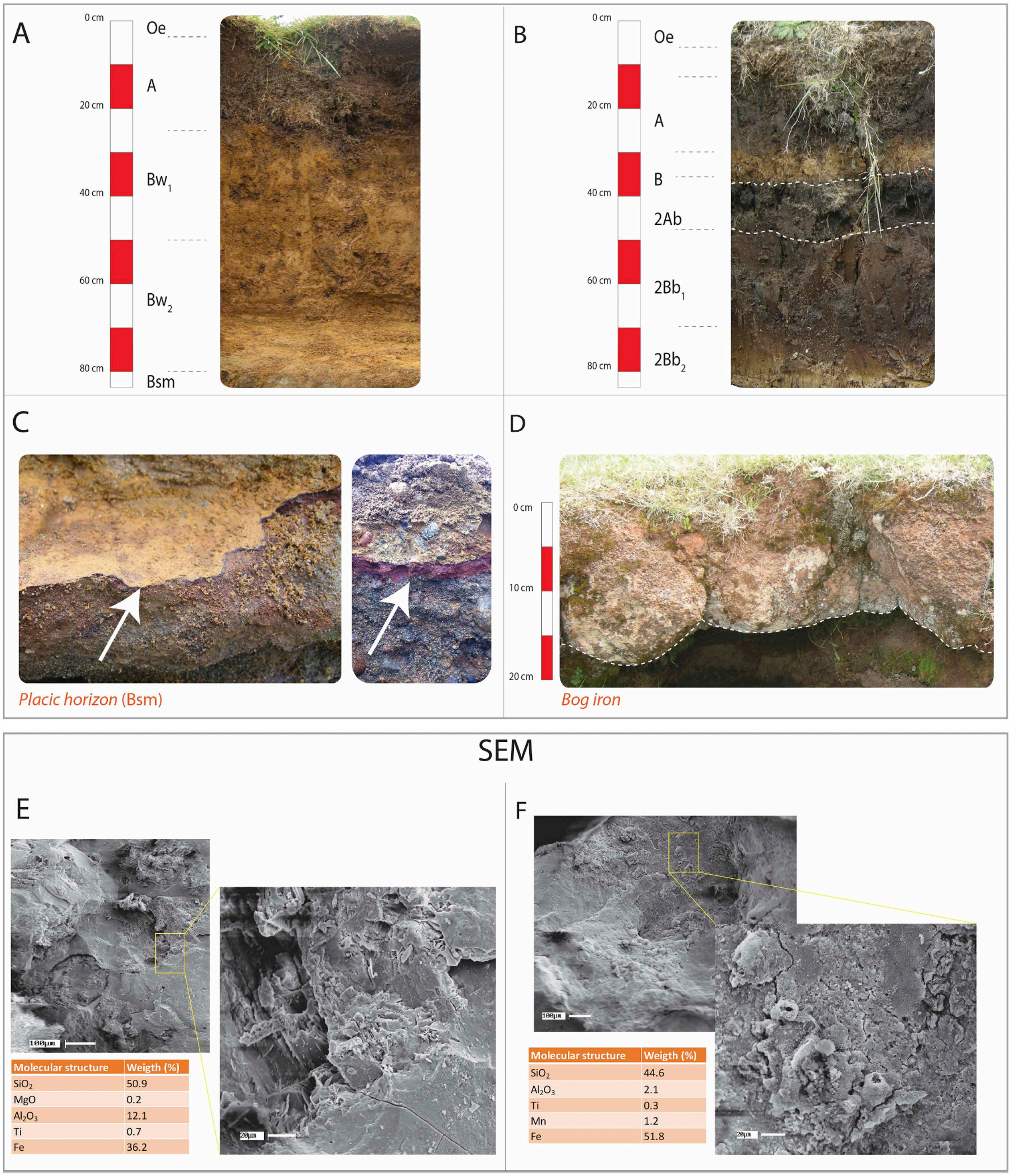

Fig. 7. A: Typical ñadi soil profile. Placic horizon is underlying 80 cm. B: Buried ñadi soil profile highlighted between dashed lines. C: White arrows indicate placic horizons over fluvi-glacial material. D: Dashed line highlight the "bog iron" in the archaeological site "Monte Verde". Below: Scanning electronic microscopy (SEM). E: placic horizon (Bsm) of Alerce soil Series. F. Bog iron from Monte Verde. Yellow square is a zoom of 20 µm in both images. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3.1. Dynamics of changes in land cover and use of ÑS

The land cover change of these ecosystems was produced as a consequence of the need for new agricultural or forestry land. The original land cover of ÑS was native forest (Lara et al., 2012), which among other functions played an important role in carbon sequestration and water conservation. However, in the Ñadi ecosystems after deforestation, in addition to agriculture, the following land uses have been introduced: i) secondary native forests (*Nothofagus dombeyi* (Mirb.) Oerst., *Drimys winteri* J.R. Forst. & G. Forst. 1776, *Saxegothaea conspicua* Lindl.), ii) forestry plantations (mainly *Eucaliptus nitens* H. Deane & Maiden), iii) naturalised grasslands (*Aira caryophyllea* L., *Holcus lanatus* L., *Agrostis capillaris* L., *Dichondra repens* J.R. Forst. & G. Forst., *Lotus uliginosus* Schkuhr) and others.

3.3.2. Degradation and recovery of eco-sociological vegetation community

Ramírez et al. (1991) indicated that such eco-sociological vegetation change, due to anthropogenic degradation, favours hemicryptophytes, which replace the phanerophytes (see Raunkiær, 1907). However, this dynamic depends on whether there are favourable[4] or unfavourable conditions in the Ñadi ecosystem, which is also a function of temperature and waterlogging conditions (the dynamics of soil

[4] Favourable conditions refer to: soil depth (> 50 cm), placic horizon at depth (> 80 cm), occasional water logging and temperate conditions. Unfavourable conditions are related to inverse characteristics (Ramírez et al., 1991).

Table 2
Chemical properties of iron cemented layers from Ñadi soils of Southern Chile, and other values of placic horizons studies in the literature.

Soil property	Unit	Placic horizon (Bsm)	Bog iron	Campbell and Schwertmann (1984)	Besoaín et al. (1992)	Luzio et al. (1992)	Palma (1993)	Hseu et al. (1999)	Lapen and Wang (1999)	Pinheiro et al. (2004)	Jien et al. (2010)	D'Amico et al. (2016)
Si_o	%	0.937	0.162		1.35–2.33	0.12–3.40						
Al_o	%	1.270	0.133	0.44–4.20	2.27–4.62	2.51	0.8–7.2	0.1–0.6	0.6–1.5	3.5–5.2	0.4–0.6	0.076
Fe_o	%	1.977	1.707	8.33–23.2	0.3–1.30	9.70	2.3–12.1	7.3–8.9	10.2–3.8	7.4–10.5	17.4–3.4	0.317
Mn_o	%	0.013	0.140									
Al_p	%	1.518	0.087		0.16–0.35		0.16–1.10		0.4–1.3	0.5–2.4	0.3–0.9	
Fe_p	%	0.680	0.723				0.05–1.7		1.0–2.7	0.4–8.5	4.3–7.6	
Mn_p	%	0.001	0.006									
Si_d	%	0.915	1.027			0.12–1.49						
Al_d	%	1.509	1.141	0.89–3.86			1.4–3.8	0.5–1.1	1.4–0.6		1.43–0.85	
Fe_d	%	16.075	26.578	13.8–33.8	0.9–1.5		4.2–29.0	10.0–11.3	6.5–4.5	7.9–11.1	32.7–13.0	0.457
Mn_d	%	0.013	0.105			0.003–4.50		0.02–0.36				
Al_o-Al_p	%	−0.248	0.046									
Fe_d-Fe_o	%	14.805	24.817									
Al_a	mg kg^{-1}	319.45	37.34									
SOC	%	0.25	0.58		0.6	3.1	1.1–5.6	0.8–2.2	1.7–4.2	2.8–5.8	2–3	
pH NaF		10.09	8.23							10.2–11.4		11.0
pH_w (1:2.5)		6.26	6.02	4.2–5.3	6.2–6.3	6.0	5.0–6.1	4.6–4.9	5.1–5.2	5.2–6.1	3.87–4.91	

temperature and water table depths are described in Dec et al., 2017). These dynamics can be defined as follows:

i) *Favourable conditions*: when the original vegetation (*N. dombeyi-Eucryphia cordifolia* Cav., 1798) is grazed, will be changed to a naturalised grassland community dominated by *A. capillaris*. If this change occurs without grazing the original vegetation is replaced by *Chusquea quila* Kunth.

ii) *Unfavourable conditions*: when the climax vegetation (*Nothofagus antarctica* (G. Forst.) Oerst. 1871), is subject to grazing, it will be replaced by *Juncus procerus* E. Mey grasslands. When no occurs, it will be replaced by *Chusquea uliginosa* Phil.

Montaldo (1977, 1990 and 1999) evaluated the recovery of the phytocenoses in anthropogenic Ñadi grassland (S 39°55′, W 72°30′). He found that in the first stage, after 10 years of livestock exclusion, there was a change in botanical composition, from an *Agrostis-Juncus* complex (Montaldo, 1974) to *Rubus ulmifolius* Schott. After 25 years of livestock exclusion there was an increased presence of *Maytenus boaria* Molina and *Myrceugenia exsucca* O. Berg., that represent a transitional stage. The intermediate species of the eco-sociological succession *D. winteri*, *Lomatia hirsuta* Diels ex J.F. Macbr. and *Luma apiculata* (DC.) Burret., appeared after 35 years of livestock exclusion (Montaldo, 1990; Ramírez et al., 1993). Under these conditions, it has been demonstrated that further 30 years are needed to reach the initial stages of climax vegetation (recovery from degraded grassland to native forest). A brief summary of these processes is given in the Fig. 8.

3.3.3. Specific land covers to specific ecosystem services

Intrinsically the ecosystem services include the soil quality concept that in its simplest definition is "*the capacity* (*of soil*) *to function*" (Karlen et al., 1997). The Ñadi agro-ecosystem was exposed to an intense land cover change in the past. Today, the expansion of cities and intensive agriculture makes the soils more prone to degradation due to their very shallow soil profiles (< 50 cm). (Ellies et al., 1993; Dörner et al., 2017). Therefore, there are problems related to the land use change, which has to be further researched as e.g. CO_2 emissions. The above, along with other greenhouse gases (GHG) was assessed in peat soils by Kechavarzi et al. (2007) and Phillips and Beeri (2008).

Also, other ecosystem services provided by ÑS as e.g. hosting of biodiversity, cultural heritage, and others could be relevant for determination of the specific use of these soils. Ramírez et al. (1996) suggested that in order to conserve the flora and fauna biodiversity, it is necessary to maintain at least 20% of the Ñadi surface area (~100,000 ha) as native forest.

Evidence of the earliest human presence in the Americas is the Monte Verde II (MV-II) archaeological site dated between 18,500 and 14,500 yr BP (Dillehay et al., 2015). MV-II is located in the Ñadi zone in southern Chile and the landscape was shaped by the fluvio-glacial Salto Chico Formation and the Monte Verde Formation was developed over Maullín river deposits and volcanic ash deposits, both during the late Pleistocene. Preservation of the MV-II archaeological site until today was possible owing to the climatic conditions that predominated during their formation. At that time the environmental wet conditions and anoxic character of the peat layer[5] (MV-5) sealed the site above the MV-6 horizon. Leaching of water to the silica-gel substratum (MV-7) sealed the site below the MV-6 horizon. Both processes resulted in the maintenance of an ideal environment for the preservation of the archaeological artefacts in MV-6 because of the low O_2 concentrations, low temperatures and wet conditions (Dillehay, 1984; Dillehay and Collins, 1988; Tuross and Dillehay, 1995).

Currently, the ÑS in this area support human settlements. MINVU (2011) indicated that the Puerto Montt-Puerto Varas region has grown rapidly with an inter-census growth rate of 36%. From 2002 to 2012 the population grew from 175,000 to 238,000 habitants. This situation is consistent especially with the areas approved for housing development that are located in the "El Tepual" sector, where the ÑS are the most frequently soil resource.

3.4. Cultivation of Ñadi soils through drainage: Techniques, management and application

Gerding et al. (2014) argued that after the land use change from secondary native forest to grasslands in the Ñadi zone rehabilitation for the expansion of agricultural land usually implies the implementation of a drainage system. The consequences on agricultural productivity and environment had not been fully investigated in this soil type as discussed in Dörner et al. (2016). Drainage in the Ñadi zone is needed to cultivate these lands because of they are subject to seasonal waterlogging (Dec et al., 2017). Luzio et al. (1992) indicated that poor drainage condition is a result of the presence of the placic horizons. However, Ellies and Mac Donald (1989) indicated that in Andisols and Ultisols the imperfect drainage is associated with soil structural properties. Dörner et al. (2016) demonstrated that in ÑS (Duric Histic Placaquands) hydraulic properties vary and as changes in structural properties play an important role in the waterlogging of ÑS where the pore continuity in deeper soil horizons decreases intensely forming the

[5] For details of soil layers see Dillehay and Collins (1988); Dillehay et al. (2015).

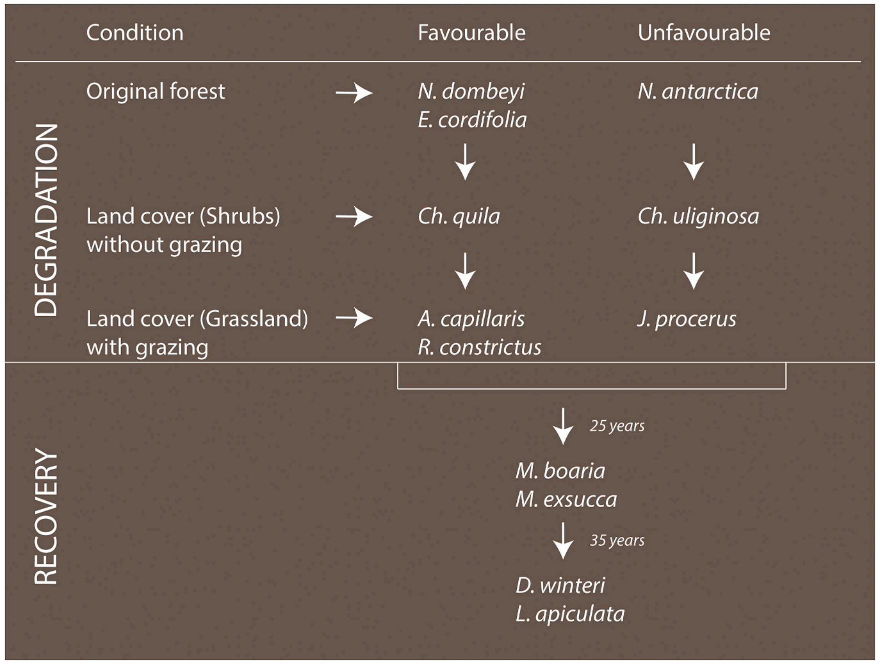

Fig. 8. Diagram of the degradation and recovery of eco-sociological community in ñadi ecosystems (Adapted from Ramírez et al., 1991).

first barrier to water infiltration.

Cultivation and the establishment of drainage systems was based on techniques used in Chile and accepted by the Chilean government as a basic management tool to improve soil properties. However, Grez (1993) stated that cultivation after drainage implies a loss of organic matter, and soil quality and an increase in hydraulic stresses (Dec et al., 2017), provoking soil shrinkage and subsidence. The authors conclude that the use of these soils should be restricted to native forest species. Drainage causes different negative consequences, e.g. soil subsidence between 30 and 40 cm, or the loss of soil organic matter between 15 and 30% (Ellies, 2001). However, changes in the water/air relationship as a result of drainage enhance the humification and mineralisation of SOC (Segnini et al., 2013; Kumar et al., 2014). Dörner et al. (2016) affirmed these findings, indicating that before the implementation of drainage systems, the land use change provoked a well-defined spatially variable reduction of soil depth, which is still not finally understood. Furthermore, the impact on soil productivity and the local environment as well as the long-term evolution of the soil due to the change in the water and thermal regimes needs further attention (for more details see also Dec et al., 2017).

Janssen et al. (2004) investigated the influence of raised beds techniques (“camellones”) on the physical and hydraulic properties of ÑS comparing tilled and non-tilled soils, under *E. nitens* plantation. They found that these techniques increased the effective soil depth and the air-filled porosity of these soils. However, the saturated hydraulic conductivity reduced up to 1 order of magnitude (100 to 10 m d^{-1}) after 24 h of steady flow indicating detrimental soil structural changes that are related to the hydrophobic properties of ÑS. Raised beds also improve the growth of *E. nitens*, because the disturbed structure in the raised-fields allows an increase of water-unsaturated soil volume enabling the roots to explore more soil volume with a higher oxygen concentration. Despite these results, the forest productivity of these ÑS sites is still marginal (Gerding, 2010), indicating, that application of this technique alone was not sufficient to improve the yield of this ecosystem considerably.

The impact of drainage on grasslands productivity in Ñadi agroecosystems was also evaluated by Teuber (1996), who indicated that it is possible to reach production levels closer to 11 Mg DM ha^{-1} by incorporating pasture improvement strategies such as: the sowing of new species, drainage and fertilisation. The grassland experienced a 113% increase in yield, and the beef body weight increased up to 88% (Jerez and Ortega, 1996). It is known that increases of dry matter production depend on soil depth and fertilisation (Pieters and Baruch, 1997), however, studies in ÑS grasslands that include the interaction on soil depth variation, drainage and fertilisation soil are scarce.

Other extensive management is related to breeding systems in ÑS. Using *Hereford* livestock in grasslands (dominated by *A. capillaris*) without fertilisation. Siebald et al. (1987) reached yield close to 5 Mg DM ha^{-1}, a beef production of 275 kg beef ha^{-1}. Steers and heifers reached mean weight of 200 kg at weaning. Sierra (1982) indicated that the ÑS show a better performance for grasslands than crops, however, this is highly dependent on the summer season. If it is dry, the yield could be decreased drastically to 2.74 Mg DM ha^{-1} in naturalised grasslands without fertilisation and irrigation (Siebald et al., 1987).

4. Discussion

4.1. Iron-cemented layers in the Chilean framework

Searching in the WoS and Google Scholar reveals that in the global context 77 studies which include effective research on placic horizons were conducted. However, nothing was found regarding for Chilean soils. This situation doesn't imply that nothing was developed, in fact, this was one of the reasons to prepare this review! Many of the Chilean studies were technical bulletins, undergraduate thesis, book chapters and even “papers” that were written in Spanish and are therefore limited especially to Latin-American readers or those who understand Spanish.

The studies of ÑS started in Chile by Díaz et al. (1958), who simply described soil profiles. They were followed by the ideas of soil formation as proposed by Alcayaga (1964). However, it was only in 1992, when in papers published in the Special Edition “Hardened Volcanic Soils, of Terra Latino Americana” the pedological process of ÑS and “fierrillo” are described by Luzio et al. (1992) and the chemical and mineralogical characterisation are carried out by Besoaín et al. (1992). This review is not only a compilation of these studies made in Chile with placic horizons, but it is also a glimpse at our scientific past for putting the efforts that soil scientist made in a global context in order to

highlight the specific behaviour and ecosystem services of these soils from southern Chile acquainted.

4.2. Formation of ÑS and "fierillo"

As was mentioned by Alcayaga (1964) the formation of ÑS occurred in wet and acidifying conditions such as a swamp. These conditions are common in the south of Chile (Fig. 3), allowing the SOC accumulation in the surface horizons in the Alerce and Calonje soil Series (Fig. 3B). The evaluated soil Series in the transect, which has more SOC, have less reactive forms of Si, Al, Fe and Mn (Fig. 4). However, the high percentage (~85%) of the variance explained by oxalate and dithionite-citrate-bicarbonate extractions in the soil surface horizons in ÑS suggest that the reactive pools come from non-crystalline materials as allophane and imogolite and hydrated oxides of iron (Fig. 5). The Al_p linkage to organic compounds have more relative participation in the reactive fraction in the Frutillar, Alerce and Calonje soil Series, however, more research is necessary to explore different extractions (e.g. $CuCl_2$ and $LaCl_3$) for determine the degree of stability of organic fractions and the mechanisms of carbon stabilization in ÑS (García-Rodeja et al., 2004; Panichini et al., 2017).

Luzio and Saavedra (1992) and Bockheim (2014), indicate that the formation of the placic horizon requires abundant precipitation (> 2400 mm year^{-1}) and rich-organic horizons that lead on the Fe mobilisation and reoxidation in the textural discontinuity. This affirmation its consistent with the SOC levels and Fe_p that we find in the Calonje soil Series (Fig. 3B, 5C), suggesting that under actual climate conditions (Fig. 3A) the chelation and translocation of Fe (Fig. 6C) occur and moves the iron towards deeper horizons for precipitate as "fierrillo".

Similar values of Fe_d were found in studies of Campbell and Schwertmann (1984) in German Podzols and by Jien et al. (2010) in Taiwanese Inceptisols. Lower values were found by Besoaín et al. (1992) in the Bsm horizon studied in Chilean Ñadi Soils (Frutillar and Alerce soil Series), a pattern that is repeated for Fe_o. Our Al_o values are lower than in other volcanic soils in Chile (Luzio et al., 1992) and in Portugal (Pinheiro et al., 2004). The highest values of Al_p and Al_d found in the Bsm studied are consistent with the values assessed by Palma (1993) in different "fierrillos" from southern Chile, reaffirming the translocation of Fe and Al linked organic compounds. In Bsm and bog iron the SOC is very low and pH is slightly acid compare to Inceptisol and Podzols of Canada (Lapen and Wang, 1999) and Inceptisols in Taiwan (Hseu et al., 1999).

4.3. New frontiers of soil science development in the Ñadi agro-ecosystems

Currently, the agricultural global scenario is dynamic and challenging. The main issue is the world food demand. Scientists calculate that in 2050 it will be necessary to feed a population of 9 billion people within the scenario of climate change. This challenge has to be faced responsibly through the intensification of sustainable agriculture (Beddington et al., 2012). This strategy can be carried out in areas with the potential for major crop expansion i.e. Latin-America and Sub-Saharan Africa (FAO, 2009). Land use change in the last 500 years in southern Chile has been very intensive, causing the replacement of 51% of native forests with agricultural land and urban areas (Lara et al., 2012) which has led to degradation of the ecosystem and to soil erosion (Ellies, 2000, 2001). Discussions how to gain the required food and clean groundwater are also ongoing since decades and include also potential and most suitable use of these ÑS soils (Grez, 1993). High subsidence potential and resilience (considered as the ability of recovery after natural or anthropic disturbances) in shallow ÑS profiles are discussed by Dörner et al. (2016) and Dörner et al. (2017). They suggest that both parameters are linked with SOC dynamics and land use. However, questions like what is the minimum soil depth for agriculture use? or the relevance of which qualitative properties of SOC in ÑS? have not been clarified.

Given the fragility of these soils (Dörner et al., 2016), and the challenge to use natural resources efficiently under the climate change scenario, we describe the range of ecosystem services which could be provided by the ÑS found in southern Chile.

4.4. Ecosystem services provided by Ñadi soils

Nowadays the ÑS ecosystem is mainly used for agriculture or forestry but there are other ecosystem services. From the 7 soil functions proposed by Adhikari and Hartemink (2016), the following can be developed further in ÑS.

i) *Biomass production*: ÑS have a great potential for biomass production for livestock feed and for forestry activities. But, it is necessary to discuss how and where that potential can be fulfilled and define the boundary conditions to be applied e.g. what is the minimal soil depth required to support forestry in a sustainable form and what is the maximum animal stocking rate that can be achieved without harmful effects on the environment. And it is necessary to consider how to use ÑS for forestry or agriculture without a reduction of the effective soil depth.

ii) *Storing, filtering and transforming water and nutrients*: because of their location in low lying land, the ÑS can be considered as regulators and accumulator; e.g. stocking SOC or some toxic elements (e.g. Al^{3+}), but also increasing water availability during the dry season.

iii) *Hosting biodiversity*: the ÑS are a reservoir of native Chilean flora and fauna and soil microorganisms. The maintenance of patches (at least 20% of original vegetation, according to Ramírez et al., 1996) in Ñadi ecosystems could be used to preserve and protect vulnerable species e.g. "Alerce" *Fitzroya cupressoides* (Molina) I. M. Johnst. (Benoit, 1989) or threatened species e.g. "Puma" *Puma concolor* L. (CONAMA, 2009). There is limited information available on the microbiology of volcanic soils and less about the Ñadi microbial community and their functions.

iv) *Platform for human activities*: in the landscape ÑS occupy flat locations, which are desirable sites for the building of roads, airports and other constructions. However, these kinds of services have to be discussed and regulated with government laws within an appropriate land use planning framework.

v) *Source of raw materials*: ÑS formed after the deposition of volcanic ashes over fluvi-glacial substratum provides gravel, which is used for construction. In specific conditions it is possible to find bog iron, but not in sufficient quantities to exploit viably.

vi) *Carbon pool*: ÑS stores large amount of SOC (near to 25%) in the first 20 cm depth. Maintaining this C pool contributes to aim of reducing atmospheric CO_2, which will help to mitigate climate change and encourages initiatives as "4 per 1000".[6]

vii) *Storing geological and archaeological heritage*: the interactions between iron, silica and peat that occur in these soils conserves archaeological artefacts. Monte Verde is one of the most important heritage archaeological sites in South America.

Finally, two questions need to be considered: a) how can we enhance the ecosystem services provided by the ÑS? and b) can we classify the ÑS according to the ecosystem services it provides and restrict land use change in relation to specific site conditions?

4.5. Minimum depth of ÑS to support a productive system

Soil depth is the most relevant limiting factor for plant growth, for biomass accumulation, and root distribution. In ÑS, the soil depth exhibits high spatial variation across the landscape (CIREN, 2003) and at the field scale (Dörner et al., 2016). The soil depth may fluctuate between 30 and 90 cm in the field depending on land use (Dörner et al.,

[6] https://www.4p1000.org/.

2016; Carrasco et al., 2017). Grez (1993) suggested that soils with depths < 50 cm shouldn't be used for agricultural purposes and Dörner et al. (2017) argued that soil depth should be related to the very low bulk density and the high potential for deformation of these soils due to the very low pre-compression stress (i.e. mechanical stability) and the high shrinkage potential. Land use change and drainage of these soils induces new and great mechanical and hydraulic stresses (Dörner et al., 2017), which can induce further soil deformation in very shallow soil profiles (Horn et al., 2007).

Dörner et al. (2016) when comparing native forests (NF) and naturalised grassland (NG) on ÑS recorded changes in physical quality indicators that determine the soil pore connectivity. It was found that under NF, medium and fine pores increase by 50% and the pores continuity index[7] (C_2) was reduced by 85% from 5 to 30 cm depth. At the same depth in NG, the pores were reduced by 38% and C_2 into 32%. This raises the question which is the main cause of poor drainage of these soils: the limited soil depth, the pore discontinuity in deeper soil horizons or both factors?

One method to improve the poor drainage conditions of ÑS is the implementation of raised beds ("camellones"), which allows a gain in soil depth and an increase in the volume of air-filled pores in the soil (Janssen et al., 2004). However, at the same time it implies the alteration of the soil pore network and probably affects the pore continuity with depth. This interaction between the soil pore network and their continuity is unclear. Further research is needed in order to determine the diffusion properties of these horizons and to understand the changes that occur in the soil architecture. One approach to the problem may be the application of x-ray computed tomography (Pagenkemper et al., 2015).

4.6. Consequences of drainage (post land use change) on soil shrinkage, SOC mineralisation and GHG emissions

Land use change of ÑS has included clear cutting of the forest and in some cases, it's burning (Haller et al., 2015). This lead to the reduction of SOC and, consequently, an increase of CO_2 in the atmosphere (Lal, 2004). In addition, ÑS could be source of other GHG emissions since under season-dependent water logging, anoxic conditions prevail, which favours denitrification processes. This increase enhances the release of N_2O and finally methanogenesis with resulting CH_4 emissions to the atmosphere (Tian et al., 2015). To reduce the waterlogging conditions ditches or mole drainage have been used, without considering the consequences for soil productivity and the environment (Dörner et al., 2016).

Montagne et al. (2009) indicated that subsurface drainage is an active agent of soil evolution. Subsurface drainage induces soil subsidence (Ellies, 2001) and promotes crack formation that favours preferential water flows through the macropores. We can expect these changes in ÑS due to the high amount of soil organic carbon, which induced a high shrinkage capacity of volcanic ash soils (Dörner et al., 2010; Dörner et al., 2017). The drainage network, formed by macropores, transports water, dissolved soil organic matter, solid particles and nutrients such as Ca, K, Mg, Na, and reduced forms of Fe and Mn (Montagne et al., 2009). In contrast the air/water relationships change due to an increased air-filled porosity, which further increases the humification rate and organic carbon mineralisation (Bouckaert et al., 2013; Segnini et al., 2013). Additionally, due to changes in the redox conditions, Fe and Mn could be translocated and precipitated forming ochreous deposits in drain lines (Montagne et al., 2009). Consequently, the drainage leads to irreversible changes in the soil in the human-life time scale. Therefore, the following questions have to be faced in order to understand the consequences of drainage of these extreme soils: i) can we consider the ÑS as a sink for CO_2?; ii) how intense are the changes of GHG emissions under seasonal waterlogging?; iii) to what extent is the formation and the movement of CH_4 and N_2O in Ñadi soil profiles dependent on water table depth?; iv) how is the microbial community changed after drainage? and v) do we need to drain the ÑS?. If yes, when can we do this? and what are the boundary conditions to conduct this kind of cultivation strategy? e.g. minimum soil depth; and what are the long-term consequences for the physical, chemical and biological properties of the soil and the environment?

[7] Pores continuity index = air permeability/air-filled porosity.

4.7. Ñadi soils in a climate change scenario

Considering the current global climate change scenario, in which temperatures are continuing to increase and precipitation is decreasing (Garreaud, 2013; Boisier et al., 2016) there are several questions to ask about the potential consequences on these extreme ÑS. Questions to be addressed include: i) how will ÑS and related ecosystem services react to the changing conditions? ii) can we still use these soils for sustainable agriculture or forestry? iii) what are the new boundary conditions for using ÑS sites and iv) can we use the ÑS without considering the use of irrigation in this new scenario?

We cannot have a single response to any of these questions due to the high spatial variability of ÑS. Even when we analyse the soils at a specific site, within a few meters different Ñadi conditions can be found with different soil characteristics, functions and ecosystem services. In addition, in the same area zones can be formed in which the soil profile is saturated and other zones that are unsaturated because of the spatial variation in soil depth, which implies that the ecosystem services related to water supply and storage will be different and consequently it will affect agronomic management.

We have to emphasize that the use of these soils is strongly related to the effective soil depth, and so we reaffirm the criteria presented by Grez (1993) suggesting that ÑS of < 50 cm in depth should be preserved, especially if we consider the current scenario of climate change.

Although initially these soils could resist changes in the climate because they have a high SOC content their SOC-dependent resilience will deteriorate over time, and if the soils are used intensively that deterioration will be more rapid. Furthermore, an increase of CO_2 emissions and a decrease of the C pool will change the qualitative properties of the soil organic matter as well as changing the microbial community, favoring the mineralisation of SOC adsorbed in clay and immobilized in microbial biomass.

5. Summary

This review provides a global context of soils with placic horizons under special consideration of the 5 Ñadi soils and 2 iron cemented layers in the Chilean volcanic ash soils (Placaquands) we considered. We describe a conceptual model of formation of these soils and using the available literature and our field work to propose a number of new research questions.

i) *Iron-cemented layers*: We found 77 studies conducted in soils with placic horizons, distributed mainly in North-America and Taiwan. However, many more studies made in Chile are exposed in this review of ÑS.

ii) *Distribution and formation*: In Chile, the ÑS are distributed between 38° to 43° S (~400 km) covering around 4250 km^2. The formation requires lithogenic iron, abundant precipitation, high SOC in the surfaces horizons and textural-structural discontinuities. These conditions are especially available in the southern part of Chile.

iii) *Fraction analyses*: The reactive pool of the soil as one moves south. Furthermore, pools extracted with oxalate and dithionite-citrate-bicarbonate can be used to separate groups of Ñadi soils.

iv) *Placic horizon and bog iron*: are mainly compounds of goethite and ferrihydrite. However, the placic horizon can have aluminium minerals such as gibbsite.

v) *Land use and ecosystem services*: ÑS of 50 cm depth should be

considered the limit of drainage boundary conditions for agricultural or forestry since the drainage of ÑS soils with < 50 cm depth has a high risk of soil degradation by settlement and C losses, which leads to significant environmental consequences e.g. CO_2 emissions. Also, the heritage cultural of Monte Verde archaeological site has been conserved thanks to the iron-cemented layers.

vi) *Questions*: In order to use these soils sustainably, we need to define the ecosystem services provided by the ÑS and highlight the ecosystem services of the ÑS. If we want to use the ecosystem services for agriculture two questions need to be answered: i) should the ÑS be drained? and ii) what are the economic, ecological and social implications of drainage? How far will drainage change these soils during climate change? Perhaps it is better to restore the native ecological condition or use the sites for non-timber forest products? We offer these questions in order to rethink the sustainable use and services of Ñadis ecosystems.

Acknowledgement

The lead author wishes to thank all the researchers and students of the “Ñadi Soils Team” for their assistance with the fieldwork, to Ruth Espinoza and Lorena Riedel for the support of laboratory analysis and for the hospitality of the landowners (Don Alfredo, Sra Elba and family). He also gives thanks to Revista Terra Latinoamericana, Víctor Gerding, Jorge Ivelic, Walter Luzio, Lorena Lagos and Christian Prat for the valuable material used to elaborate this review. He also thanks the National Commission for Scientific and Technological Research (CONICYT) for supporting the doctoral studies (Scholarship N° 21140263) and the internship of Dr. (c) Zúñiga in the “Institut für Pflanzenernährung und Bodenkunde at Christian Albrechts University zu Kiel”. Dr. José Dörner thanks the Alexander von Humboldt Foundation for the Grant “Georg Foster Fellowship for Experienced Researchers” which allowed a research stay at the Christian Albrechts University zu Kiel. We are pleased to thank the National Fund for Scientific and Technological Development (FONDECYT) N° 1130546 for funding the research project.

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